Boronate-functionalized polypyrrole as a new fluoride sensing material

M. Nicolas, B. Fabre* and J. Simonet

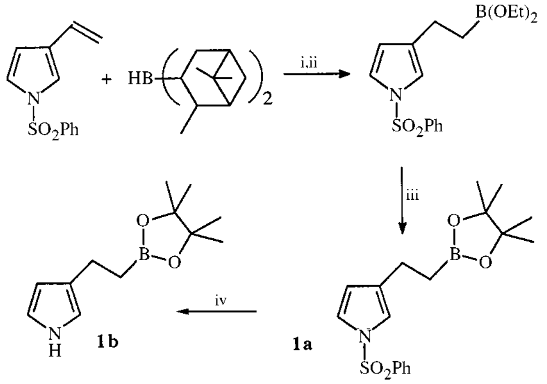
Laboratoire d'Electrochimie Moléculaire et Macromoléculaire (Unité Mixte de Recherche n°6510 associée au CNRS), Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France. E-mail: fabre@univ-rennes1.fr

Received (in Cambridge, UK) 25th June 1999, Accepted 8th July 1999

The anodic oxidation of boronate-substituted pyrrole led to a fluoride anion-responsive electroactive polymer film.

The modification of the electrochemical response of a system in the presence of a specific ion or molecule can be considered as a recognition event. In the case where such a system is deposited onto an electrode surface, this mode of recognition can be exploited for the construction of electrochemical sensors. As an example, numerous recent reports have focused on the sensing properties towards cations of some polyether or crown ether functionalized redox-active conjugated polymers.[1–7] In contrast, anion recognition by this class of polymers derivatized with a suitable receptor has been much less developed.[8,9] We have tested a novel route to anion-responsive electrodes based on a conjugated polymer substituted by a boronate group. Here, the boron-containing moiety was used as a sensing element owing to the strong interaction of this heteroatom with hard bases like fluoride giving rise to specific orbital changes from sp^2 to more stable sp^3. So, the possible electronic and/or conformational changes induced by the boron–fluoride binding could be detected from the modification of the electrochemical response of the conjugated polymer. Although numerous boronic acid-based anion and sugar receptors have been developed by Shinkai and co-workers,[10–13] their immobilization onto an electrode surface has not been investigated so far. The incorporation of boron atoms in the backbone of conjugated polymers has already been described,[14,15] but in our case we chose to attach the boronate group to the conjugated polymer by a spacer of appropriate length.

To achieve this purpose, conjugated polymer films were electrodeposited in one step onto a platinum (diameter 1 mm) electrode surface *via* the anodic oxidation in MeCN of the functionalized pyrrole. 1-(Phenylsulfonyl)-3-vinylpyrrole was synthesized in three steps from 1-(phenylsulfonyl)pyrrole using literature procedures.[16,17] Hydroboration with diisopinocampheylborane[18] (Ipc$_2$BH) prepared from (+)-α-pinene and borane–dimethyl sulfide complex gave the diethyl boronate derivative (Scheme 1). Treatment with pinacol gave **1a** as a colorless oil in 23% overall yield after purification by column chromatography (CH$_2$Cl$_2$). This was deprotected electrochemically at −2.45 V (*vs.* 10^{-1} M Ag$^+$/Ag) using pyrene as a redox mediator to give **1b** (yield 58%).†



Scheme 1 *Reagents and conditions*: i, Ipc$_2$BH (1.2 equiv.), THF, −40 °C, then addition of the vinylated compound, room temp., 24 h; ii, acetaldehyde (10 equiv.), 0° C, 24 h; iii, pinacol (1 equiv.) in THF, room temp., 24 h; *iv*, pyrene (20%), reduction at −2.45 V (*vs.* Ag$^+$/Ag) in MeCN + 10^{-1} M Bu$_4$NClO$_4$.

The electropolymerization of **1b** (10^{-2} M) was carried out in thoroughly dried MeCN containing 10^{-1} M Bu$_4$NPF$_6$ as the supporting electrolyte. The doped film was potentiodynamically electroformed with an anodic limit close to the irreversible oxidation peak potential of monomer, *e.g.* 0.75 V [Fig. 1(*a*)]. Its electrochemical response in an hydroorganic medium[19] (H$_2$O–MeCN) showed a stable reversible redox system at −0.11 V *vs.* SCE (ΔE_p = 40 mV at 100 mV s^{-1}) corresponding to the p-doping/undoping process [Fig. 1(*b*)]. The doping level deduced from the cyclic voltammetry curve was found to be in the range 0.20–0.30 depending on the film thickness.

The addition of KF led to the decrease of this system together with the emergence of a new redox system at −0.37 V, the magnitude of which increased with F$^-$ concentration. For a film

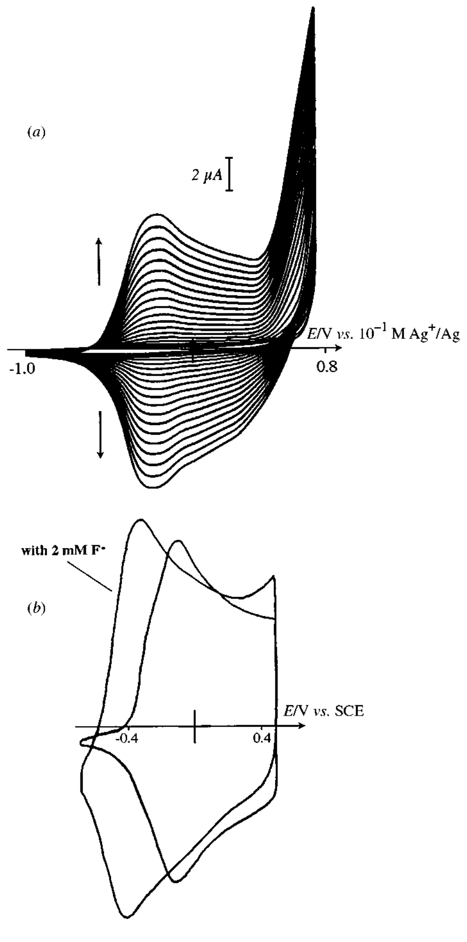


Fig. 1 (*a*) Successive cyclic voltammograms of **1b** (10^{-2} M) in MeCN + 10^{-1} M Bu$_4$NPF$_6$ (final electropolymerization charge: 70 mC cm^{-2}). (*b*) Electrochemical response of corresponding poly(**1b**) in H$_2$O–MeCN (1:1 v/v) + 5 × 10^{-1} M LiClO$_4$ in the absence and presence of 2 mM KF. Potential scan rate: 100 mV s^{-1}.

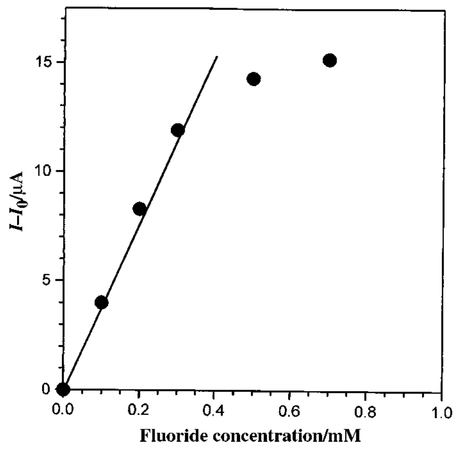


Fig. 2 Calibration curve for F$^-$ in H$_2$O–MeCN (1:1 v/v) + 5 × 10^{-1} M LiClO$_4$ obtained with a poly(**1b**)-coated platinum (8 × 10^{-3} cm^2) electrode (electropolymerization charge: 280 mC cm^{-2}). I and I_o are the currents measured at −0.42 V on the voltammetric curves (100 mV s^{-1}) in the presence and absence of KF, respectively.

electropolymerized using 70 mC cm^{-2}, only the second system was observed for a large F$^-$ concentration, *e.g.* 2 mM [Fig. 1(*b*)]. It must be pointed out that the electrochemical response of poly(**1b**) was not changed when F$^-$ was replaced by Cl$^-$ or Br$^-$ up to a tested concentration of 20 mM. Moreover the interaction with F$^-$ was specific for the boronate-containing polymer, as the voltammetric response of an unfunctionalized polymer film was found to be unmodified in the presence of this anion. Thus, all these results are consistent with a selective electrochemical recognition of F$^-$ by poly(**1b**). The negative shift of the redox potential indicates that the F$^-$ bound polymer was easier to oxidize. Such a result could be explained by a stabilization of F$^-$ bound to the boron atom by the positive charges along the oxidized polymer backbone. The effect of the F$^-$ concentration on the current intensity of the system assigned to the F$^-$ bound polymer is shown in Fig. 2. As can be seen, an initial linear plot at low F$^-$ concentrations ($<$ 0.4 mM) is followed by a plateau for larger concentrations indicating that all the binding sites in the film were occupied. The slope and the linearity range of the first part were found to be dependent on the film thickness. As a matter of fact, the sensitivity to F$^-$ was higher for thin films, as already observed for other sensory materials.[20]

Finally, this work constitutes a rare example of functionalized conducting polymer-based selective anion recognition. Some parameters, such as the film thickness, and the nature and length of the spacer arm between the monomer unit and the boron site, must be now optimized in order to obtain sensitive detection operating over a large F$^-$ concentration range.

Drs M. Vaultier, J.-F. Pilard and G. Marchand are fully acknowledged for their help in the synthesis of monomers. The 'Région de Bretagne' is also acknowledged for a research grant to one of the authors (M. N.).

Notes and references

† *Selected data* for **1b**: δ_H(CDCl$_3$) 1.04 (t, 2 H), 1.15 (s, 12 H), 2.55 (t, 2 H), 6.11 (dd, 1 H), 6.48–6.60 (m, 2 H), 8.01 (s, 1 H); δ_C 21.60, 25.22, 83.38, 108.66, 114.94, 117.90, 126.74.

1 B. Fabre and J. Simonet, *Coord. Chem. Rev.*, 1998, **180**, 1211.
2 T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.
3 P. Bäuerle and S. Scheib, *Adv. Mater.*, 1993, **5**, 848.
4 H. Korri Youssoufi, M. Hmyene, A. Yassar and F. Garnier, *J. Electroanal. Chem.*, 1996, **406**, 187.
5 A. Ion, I. Ion, A. Popescu, M. Ungureanu, J. C. Moutet and E. Saint-Aman, *Adv. Mater.*, 1997, **9**, 711.
6 L. M. Goldenberg, I. Lévesque, M. Leclerc and M. C. Petty, *J. Electroanal. Chem.*, 1998, **447**, 1.
7 F. Sannicolo, E. Brenna, T. Benincori, G. Zotti, S. Zecchin, G. Schiavon and T. Pilati, *Chem. Mater.*, 1998, **10**, 2167.
8 P. D. Beer, *Acc. Chem. Res.*, 1998, **31**, 71.
9 M. M. G. Antonisse and D. N. Reinhoudt, *Chem. Commun.*, 1998, 443.
10 T. D. James, K. R. A. Samankumara Sandanayake and S. Shinkai, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1910.
11 C. R. Cooper, N. Spencer and T. D. James, *Chem. Commun.*, 1998, 1365.
12 H. Yamamoto, A. Ori, K. Ueda, C. Dusemund and S. Shinkai, *Chem. Commun.*, 1996, 407.
13 C. Dusemund, K. R. A. Samankumara Sandanayake and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1995, 333.
14 R. J.-P. Corriu, T. Deforth, W. E. Douglas, G. Guerrero and W. S. Siebert, *Chem. Commun.*, 1998, 963.
15 N. Matsumi, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 1998, **120**, 5112 and 10 776.
16 M. Kakushima, P. Hamel, R. Frenette and J. Rokach, *J. Org. Chem.*, 1983, **48**, 3214.
17 R. Settambolo, R. Lazzaroni, T. Messeri, M. Mazzetti and P. Salvadori, *J. Org. Chem.*, 1993, **58**, 7899.
18 I. Paterson, J. M. Goodman, M. A. Lister, R. C. Schumann, C. K. McClure and R. D. Norcross, *Tetrahedron*, 1990, **46**, 4663.
19 In water, the electroactivity of poly(**1b**) was weaker and less reversible than that exhibited in organic electrolyte, probably owing to the presence of the hydrophobic pinacol moiety.
20 See for example: A. C. Ion, J. C. Moutet, A. Pailleret, A. Popescu, E. Saint-Aman, E. Siebert and E. M. Ungureanu, *J. Electroanal. Chem.*, 1999, **464**, 24.

Communication 9/05136H